In re Application of
Richards et al.

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Serial No.: **10/643,062**

Filed: **August 18, 2003**

For: **Method of Photochemically Removing
Ammonia from Gas Streams**

Docket No: **4094-009**

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PATENT PENDING

Examiner: Ms. Edna Wong

Group Art Unit: 1753

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DECLARATION UNDER RULE 1.132

I, John R. Richards, reside at 2605 Tanglewood Drive, Durham NC, USA and am a co-inventor of United States patent application serial no. 10/643,062 filed August 18, 2003 and entitled "Method of Photochemically Removing Ammonia from Gas Streams". I declare as follows:

1.   I am a chemical engineer with thirty-eight years of experience in air pollution control engineering. I have bachelors degrees from Penn State University in Chemical Engineering and in Chemistry, and Masters and Ph.D. degrees in Environmental Engineering from the University of North Carolina at Chapel Hill. My graduate work concerned the use of photochemistry for air pollution control. I have worked extensively with the portland cement, utility and industrial power generation, pulp & paper, chemical, and aggregates industries on air pollution control equipment performance optimization and diagnostic testing. I was previously employed by the U.S. EPA and several engineering consulting firms. As an EPA contractor, I developed seven

of the major courses concerning air pollution control for the U.S. EPA Air Pollution Training

Institute. I have presented these courses in more than forty states. Based on this educational

background and my industrial and regulatory agency experience, I am qualified to provide a

technical opinion regarding the patents of Stevens and Kupper.

2.   I have reviewed the present patent application, the claims that are presently pending

in the case, and the office action dated January 31, 2006. I have also studied the Stevens and

Kupper et al. patents.

3.   The gas streams addressed in Stevens does not contain ammonia having a

concentration less than 40 ppm. Based on chemical reactions (2) and (3) in Stevens (Column 2,

lines 21-24), it is clear that the process requires an ammonia/nitrogen oxides concentration ratio of

approximately 1 in order to achieve NO_x reduction. This is indicated by the fact that one NH_2

radical is needed to react with each NO and each NO_2 molecule. Nitrogen oxides (Nitrogen oxides

include nitric oxide, "NO" and nitrogen dioxide NO_2.) concentrations in fossil fuel-fired boilers, kilns,

and furnaces are in the range of 120 to 1,200 ppm. An equivalent concentration of ammonia must

be added to the gas stream in order to react with the NO_x compounds. A concentration of 120 ppm

is approximately equal to 5×10^{-6} mols/l (more commonly stated as gram moles/liter or simply

moles/liter). A concentration 1,200 ppm is equivalent to 5×10^{-4} moles/liter.

> "Desirably, in the process of the present invention the concentration of NH_3 present in the mixture that undergoes photolysis is in the range from about 5×10^{-6} to about 5×10^{-3} mol/l. With concentrations of NH_3 below about 5×10^{-6} mole/l, the efficiency of the removal of NOx and/or SO_2 tends to be impaired and undesirably prolonged exposure to the ultraviolet radiation is required to achieve satisfactory degrees of removal of the undesired NOx and/or SO_2 material." Stevens, Column 3, Lines 35-44

Clearly, Stevens is teaching that at a concentration below 5×10^{-6} mol/l, his process is

"impaired" and requires "undesirably prolonged exposure." These statements are entirely

consistent with the stoichiometry (reaction ratio) of the reactions he is initiating by the photolysis of

ammonia.

It is also important to note that Stevens must use ammonia in the concentration range of 5×10^{-6} to 5×10^{-3} (120 to 12,000 ppm) in order to achieve sufficient light absorption. Stevens relies entirely on the photolysis of ammonia in accordance with Stevens reaction 1 (Column 3, line 15) to initiate the various chemical reactions that result in the destruction of NO and NO_2. As indicated by Stevens, the absorption of light is a strong function of the concentration of the compound photolyzed (see parameter "c" in the exponential term of the Beer's Law Equation shown in Stevens Column 3, line 13). The fraction of the UV light absorbed increases as the value of "c" increases. If there is an insufficient ammonia concentration, then the fraction of light absorbed is small, and the process is inoperative. Stevens recognizes this limitation and specifies that a very high ammonia concentration must be created by injecting sufficient ammonia to achieve a concentration range of 5×10^{-6} to 5×10^{-3} moles/liter. My process is fundamentally different in that (1) the chemical reactions are initiated by the photolysis of NO_2, ozone (O_3), and hydrogen peroxide (H_2O_2), instead of ammonia, and (2) no ammonia is photolyzed in the spectral range specified in the claimed invention. It is important to note that the single most fundamental design characteristic of a photochemical process is the chemical compound or compounds that are used to absorb the light necessary to initiate the intended chemical reactions. Stevens uses ammonia to absorb ultraviolet (UV) light. My process uses NO_2, O_3, and H_2O_2 that is present and is formed in the gas stream to absorb UV light.

4. In the Stevens process, ammonia is continuously added. Ammonia must be added to sustain UV light absorption and the NH_2 radical reactions with both NO and NO_2 to yield N_2 as indicated by Stevens Column 1 lines 13 – 23. No ammonia is added in my process.

5. There is no disclosure in Stevens that the gas stream includes an initial ammonia concentration of less than 40 ppm. Stevens makes no disclosure as to the initial ammonia concentration of his gas stream. Stevens does not teach that the ammonia concentration in the effluent gas stream of an industrial process has an ammonia concentration of less than 40 ppm.

What Stevens does teach is that during the process of treating the gas stream, ammonia is continuously added for the purpose of removing SO_2 and NO_x.

6. Stevens does not teach maintaining NO_x in the gas stream. Stevens' process is designed to destroy NO_x. There is no teaching or suggestion in Stevens to maintain a NO_x concentration or to operate below a maximum NO_2/NO ratio in the gas stream. Destroying NO_x on the one hand and maintaining a NO_x concentration in the gas stream on the other hand are opposite and cannot be reconciled.

Stevens does not teach maintaining the NO_x concentration in the gas stream at a concentration level sufficient to support the claimed free radical reactions. In fact, it is clear from the chemical reactions specified by Stevens that there is no dependence on NO_x concentration to sustain the reactions intended by Stevens. In Stevens, the rate of reaction of NO and NO_2 is controlled entirely by the photolysis of ammonia as specified in Reaction 1 (Stevens Column 1, Line 15). In the case of the present claimed invention, the photolysis of nitrogen dioxide, ozone, and hydrogen peroxide initiates a set of hydroxyl and hydroperoxy free radical reactions. The NO_x concentration is maintained at a level in the gas stream to support the formation of these particular free radical reactions. There is no teaching of such in the Stevens patent. That is, the Stevens patent does not maintain a sufficient NO_x concentration to support these free radical reactions.

It is important to note that Stevens teaches the destruction of <u>both</u> NO and NO_2 to yield N_2 as indicated in Stevens reactions 2 and 3 (Column 1, Lines 21-24). This is logical in Stevens because it is his intent to reduce NO_x (NO_x is the sum of NO and NO_2) to a low level. In my process, I am specifically not trying to reduce NO_x. Instead, I am simply converting NO to NO_2 in order to provide the highest possible concentration of NO_2 for the absorption of UV light. Recall, that unlike Stevens, my process relies on the absorption of UV light by NO_2, O_3, and H_2O_2. It is well established that photochemical reactions of the type intended in my process go through highly predictable concentration-time profiles whether these reaction occur in seconds as part of the intended industrial processes at high concentration, or these reactions occur at much lower

concentrations over periods of hours as atmospheric reactions in urban areas. These

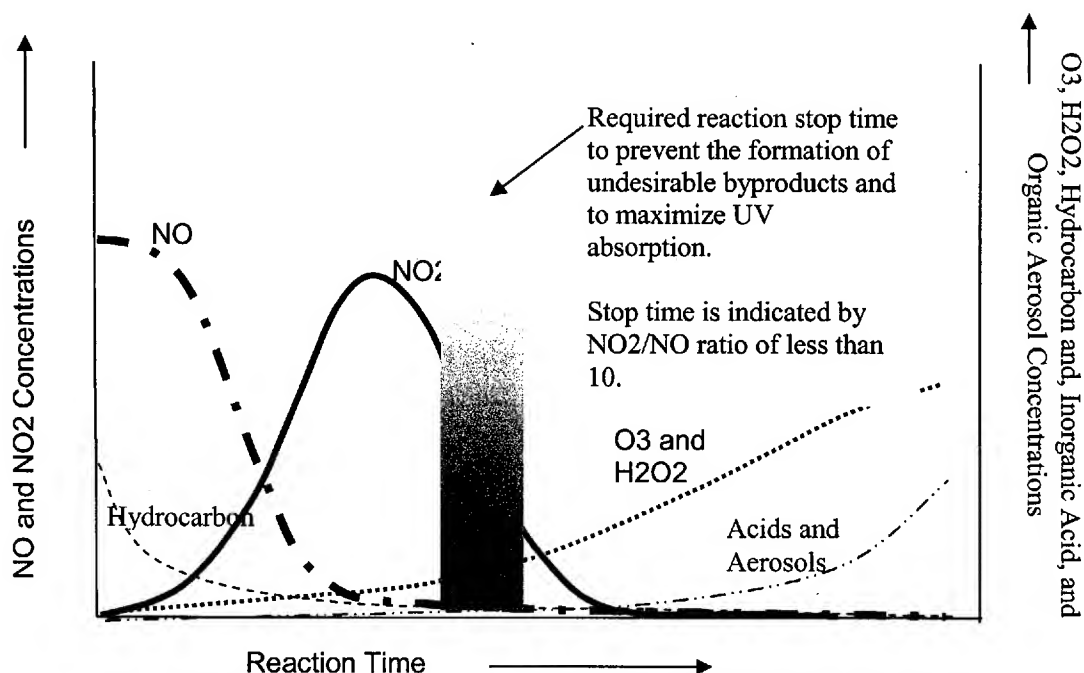concentration-time profiles are illustrated below in Figure 1.

Figure 1. Concentration - Time Profiles for Photochemical Reactions Initiated in the Spectral Range of 230-370 nm and Involving NO_x and Hydrocarbon Containing Industrial Gas Streams and Involving Typical Urban Atmospheres.

As indicated in Figure 1 above, the gas stream entering the process is primarily in the form

of NO with only a small concentration of NO_2. During UV irradiation, NO_2 absorbs UV light in the

230 to 370 spectral range, which results in a set of reactions that form additional NO_2, O_3, and

H_2O_2. While the concentrations of NO_x remain relatively high, the O_3 and H_2O_2 quickly react to

form additional hydroxyl and hydroperoxy radicals. If the reaction time is too long, undesirable

reaction products can form. In the case of urban atmospheres, these undesirable byproducts are

the constituents of smog. In the claimed process, these undesirable byproducts would be a set of

contaminants that would require additional air pollution control systems to prevent their release to

the atmosphere.

It is well established in urban photochemical smog chemistry that it is not possible to stop the chemical reactions and that undesirable byproducts, namely light scattering acids and aerosols, form. In my process, photolysis is conducted in a manner that stops the reactions immediately after the NO_2 concentration peak is reached and before adverse byproducts can form. The continuing presence of NO_2 and a lesser amount of NO is essential. This is an important aspect of my process. Stopping the reactions before a maximum NO_2/NO ratio of less than 10 is reached is fundamentally important. As indicated by this ratio, as the concentration of NO approaches zero, the value of the ratio increases. At a concentration ratio less than 10, there remains sufficient NO and NO_2 to completely suppress the formation of undesirable byproducts. This is certainly not obvious in Stevens. In fact, Stevens teaches the high efficiency reduction of NOx, and this nearly complete destruction of NO and NO_2 would allow the very byproduct formation reactions that my process is capable of avoiding.

As stated earlier, the most fundamental characteristic of a photochemical process is the species used to absorb light and thereby initiate the intended chemical reactions. In this regard, Stevens and my process are entirely different. The second most important design characteristic of a photochemical process is the means used to stop the reactions. In my process, the maximum NO_2/NO concentration ratio is used as a means to stop the reactions so that only the intended reaction, namely the oxidation of ammonia, is achieved without the formation of undesirable byproducts. Stevens does not teach any means to stop the reactions that he initiates. He is clearly attempting to drive the reactions to completion and then capture the wide variety of reaction products in a wet scrubber or similar control device.

7.   The Examiner maintains that it would be obvious to modify the spectral range of Stevens to include UV light in the spectral range of 230-370 nanometers. The Examiner indicates that there is some tendency during the Stevens process for the formation of hydrazine. Then the Examiner states that it would be obvious to modify the Stevens process to include UV light in the 230-370 nanometers spectral range to deal with hydrazine.

A person of ordinary skill in the art would not be motivated to modify the spectral range of Stevens. As indicated in Stevens (Column 8, Lines 28 to 38), the extinction coefficient (often termed "absorption coefficient" or "absorption cross-section") decreases substantially from 193 nm to 213.9 nm. As indicated in the UV absorption spectra of hydrazine published by Vaghiani, the absorption coefficient rapidly decreases as the wavelength increases toward 230 nm and is essentially at zero above 250 nm. It is apparent from the data provided by Stevens in Table 2 (Column 8) and in the text that he is destroying hydrazine by causing the direct photolytic dissociation primarily in the spectral range less than 220 nm. It is not obvious from Stevens that a photochemical process operating in the 230 to 370 nm range can initiate free radical reactions that result in the oxidation of ammonia while retaining sufficient NO_x in the form of NO_2 to sustain UV absorption and prevent formation of undesirable byproducts.
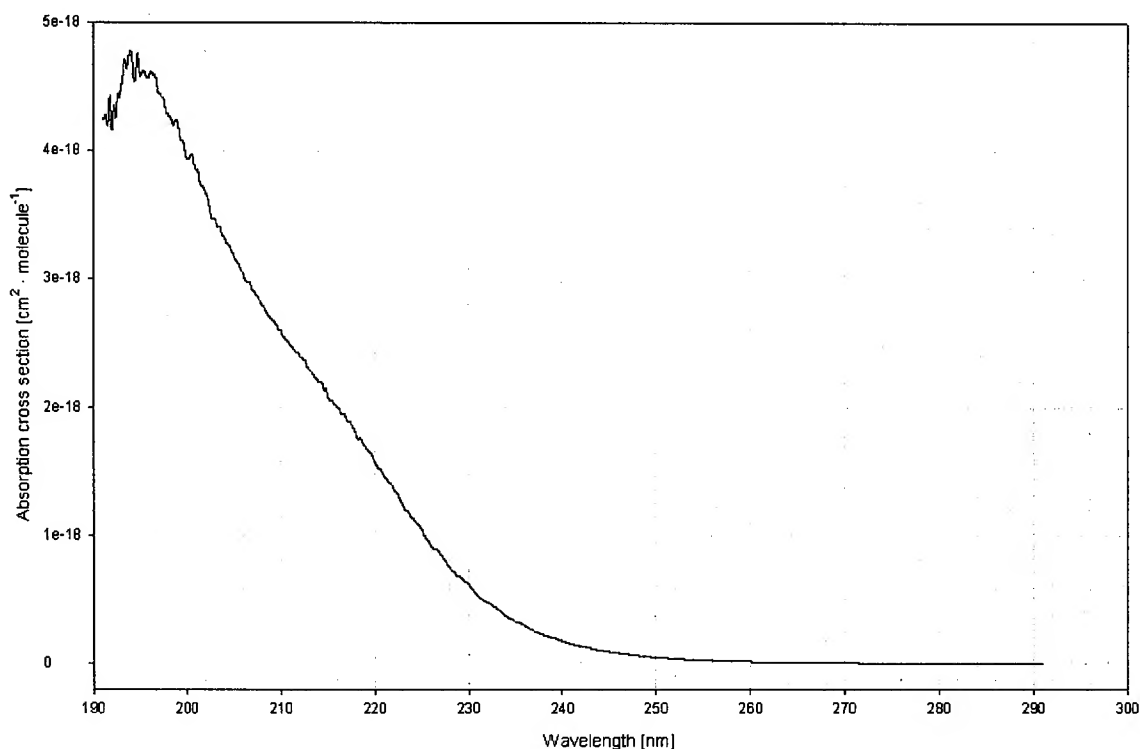
Absorption cross sections of hydrazine N_2H_4 at 296 K,
Vaghjiani, J. Chem. Phys. 98 (1993) 2123

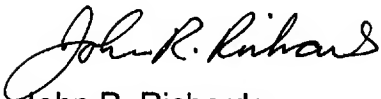Figure 2. UV Light Absorption Spectra of Hydrazine

It is clear from Stevens (Column 2, Lines 52 to 55 and Column 8, Lines 28 to 38) that the irradiation of a gas stream in the spectral range of 230 to 370 nm would result in essentially zero photolysis of ammonia and zero formation of the hydrazine formed due to the photolysis of ammonia. Ammonia does not absorb UV light in this spectral range; therefore, the photochemical reactions that form amino radicals would not occur. Without the photolysis of high concentrations of ammonia to yield high concentrations of amino radicals, hydrazine would not form. These facts alone would dissuade any person knowledgeable in photochemical control systems from altering the spectral range. It is also clear from Stevens that the irradiation of any gas stream with hydrazine in the spectral range of 230 to 370 nm would result in exceedingly low rates of hydrazine destruction.

It is important to note that Stevens clearly teaches a photochemical process that is entirely dependent on irradiation of ammonia in the extremely high energy spectrum less than 220 nm and that relies almost entirely on UV irradiation in this same high energy spectrum for the destruction of highly toxic hydrazine formed due to the extremely high concentration of ammonia created by the intentional addition of ammonia. Ultraviolet light-based photochemical processes can be divided into three main categories: (1) those that use moderate-to-low energy UV light above 220 nm, which is not capable of dissociating ammonia, oxygen, and/or water vapor, (2) those that use high energy light below 220 nm, which does result in the dissociation of oxygen and/or water vapor, and (3) those that use photocatalytic materials. Neither my process nor Stevens involves the use of photocatalysts. My process is clearly the first type of process that uses moderate-to-low energy UV light. The process described by Stevens is clearly the second type, which involves high energy UV light sufficient to dissociate ammonia, oxygen, and/or water vapor and, therefore, creates the potential for significant health effects if stray light escapes into lamp housings, lamp purge air streams, or other occupied areas. Manufacturers of conventional UV lamps use lamp envelopes that prevent the emission of light below 220 nm to avoid the highly significant health effects that can be associated with the high energy UV spectra below 220 nm. It is not a minor design change

or an obvious operational change to go from high energy UV light in the less than 220 nm range to the moderate-to-low energy UV light in the spectral range of 230 to 370 nm. There are significant safety and health issues involved with these two quite different UV light spectral ranges.

8.   A person of ordinary skill in the art would not be motivated to combine the teachings of Kupper et al. to Stevens. Stevens has nothing whatsoever to do with a cement manufacturing process. There is nothing in either Kupper et al. or Stevens that would suggest to a person of ordinary skill in the art a reason to convert Stevens into a cement manufacturing facility or process. Stevens teaches the reduction in NO_x and SO_2 emissions based on the addition of ammonia to a concentration sufficient to absorb sufficient UV light in the high energy spectral range and to cause the formation of NH_2 radicals. There is nothing in Stevens that states or even indirectly suggests that there is an intent to reduce the ammonia already present in the gas stream before the photochemical process. Kupper teaches a NO_x reduction process for cement kilns involving the adsorption of ammonia in one or more adsorption units followed by the release of the ammonia into a high temperature gas stream to react with NO_x to form N_2. It is well known that the gas phase reaction between NO_x and NH_3 begins to occur above 1600°F and continues to approximately 2100°F above which NH_3 is simply oxidized to form additional NO_x. Kupper (5,219,544) does not teach a photochemical process and, is therefore, entirely different from Stevens and my process. Kupper requires the use of adsorption vessels, which are not required in my process. Kupper uses gas phase reactions that are generally termed "selective non-catalytic reduction reactions" that involve NO_x and NH_3 but are otherwise completely different from photochemically initiated free radical reactions.

I hereby declare under penalty of perjury that to the best of my knowledge and belief all of the foregoing statements are true.

John R. Richards